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Determination of the Solubility of Thorium Hydroxide

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Thorium nitrate solution of 3×10^{-3} mole was adjusted to 5.5~8.0 in pH value with sodium hydroxide and was filtered. The amounts of thorium in the filtrate was determined with the colorimetric method using *o*-arsonophenylazo-chromotropic acid as a colorimetric reagent. The solubility of thorium hydroxide was estimated as follows:

pH=3.75; Th=4.32 mg/liter, pH=4.30; Th=590 μ g/liter,

pH=4.70; Th=347 μ g/liter, pH=5.40; Th=68.5 μ g/liter,

pH=6.05; Th=43.5 μ g/liter, and pH=7.10; Th=32.7 μ g/liter.

Other factors which control the solubility of thorium hydroxide were discussed.

INTRODUCTION

In the course of investigating the trace amounts of thorium in natural waters, exact informations about the thorium ion in solution: hydrolytic behaviours of thorium ion, formation and precipitation of colloidal thorium hydroxide, and solubility of thorium hydroxide, have been required.

There are also considerable discrepancies among the literatures regarding the solubility of thorium hydroxide¹⁾, and it has been assumed that these disagreements are mainly due to the complicated behaviours of hydrolytic species of thorium, especially of colloidal thorium hydroxide, in solution²⁾.

The purpose of this report is the estimation of solubility of thorium hydroxide with respect to the hydrolytic behaviours of thorium in solution. The experiments are divided into two parts: the first is the estimation of hydrolytic species of thorium using the pH titration method, and the second is the determination of solubility of thorium hydroxide with the colorimetric method.

EXPERIMENT 1

pH Titration of Thorium Ion

Preparation of reagents. Carbonate-free sodium hydroxide of 0.1*N* was used as a titrant and the customary precautions were taken during its preparation and storage. One-hundredth mole of thorium solution was prepared from the pure nitrate salt, containing 2.32 g of thorium ion per liter of solution. The acidity of thorium solution was adjusted to about pH 2.5 with nitric acid (to prevent the hydrolysis), and stocked in a polyethylene bottle.

Titration procedures. Twenty ml of thorium nitrate solution was titrated with 0.1*N* sodium hydroxide solution under vigorous stirring. pH change of

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this titration system was measured with a glass electrode pH meter.

RESULTS

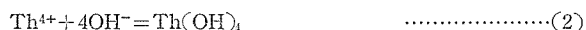
pH value of the thorium solution, which was 2.5 in pH value at the beginning of the titration, rose gradually on adding the sodium hydroxide. At pH 3, the solution began to be cloudy and its turbidity increased with successive addition of titrant. At pH 6.5, this turbidity changed into flocky precipitation and the pH of the solution increased promptly about this pH value.

The results of this titration were illustrated in Fig. 1. The scale of ordinate was graduated in pH value and that of abscissa was graduated according to the following equation :

$$n = \text{equivalents OH}^- \text{ added/mole of thorium} \dots\dots\dots(1)$$

where n was referred to the hydroxyl number of the system or the degree of neutralization.

Such titration can be considered as a kind of acid-base titration as if the thorium ion plays tetravalent acid :



On examining the titration curves, some interesting phenomena, that differed from ordinary acid-base titration system, were observed. In ordinary titration system, if one repeat the titration under the same condition, the identical titration curve should be obtained. In this case, however, the identical curve could not be always obtained. Besides these, the shape of the titration curve seemed to be affected by the velocity of the titration process which was neglected in the ordinary titration system. When the titration was carried out rapidly, the shape of titration curve had such tendency as illustrated by the curve (a) in Fig. 1. If the titration was carried out rather slowly, the shape of titration

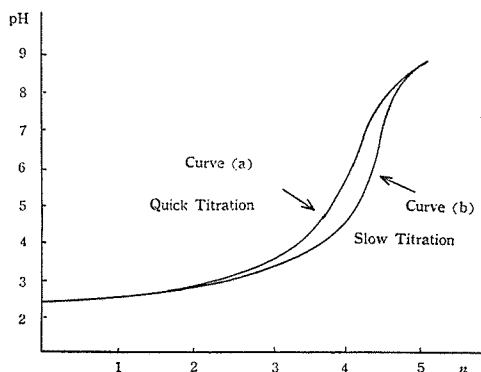


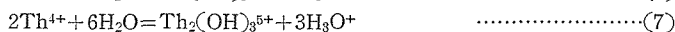
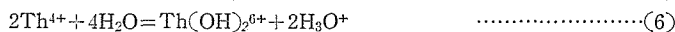
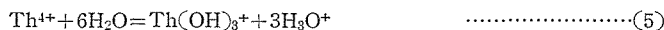
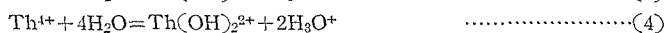
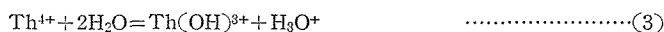
Fig. 1. Time effect of the pH titration of thorium ion.

curve had another type as the curve (b). We will refer to "time effect" of titration curve for this phenomenon. Next event was the "pH shifting" phenomenon : as this phenomenon was directly concerned with the formation of the titration curve, pH of the titration system shifted to lower pH value when the titration was stopped during the titration process.

The previous results lead to the conclusion that the reaction of thorium ion to hydroxyl ion is not so simple as equation 1 but more complicated.

DISCUSSION

Hydrolytic species of thorium. Concerning the hydrolytic species of thorium in aqueous solution, Kraus and Holmberg³⁾ have investigated the hydrolysis of thorium by the measurements of emf in perchlorate and chloride solutions using a glass electrode and indicated the existence of monomeric species $\text{Th}(\text{OH})^{3+}$, $\text{Th}(\text{OH})_2^{2+}$, and $\text{Th}(\text{OH})_3^+$ and dimeric species $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_2(\text{OH})_3^{5+}$, in the appropriate range of pH. The equilibria of hydrolysis are as follows:



As hydrolysis proceeds, higher polymeric species must be also formed. For this polymers, Lundgren⁴⁾ have indicated the existence of $[\text{Th}(\text{OH})_2]_n^{2n+}$ by the X-ray diffraction measurements.

Kraus and Holmberg also evaluated the hydroxyl number of thorium as a function of acidity. These results were illustrated in Fig. 2.

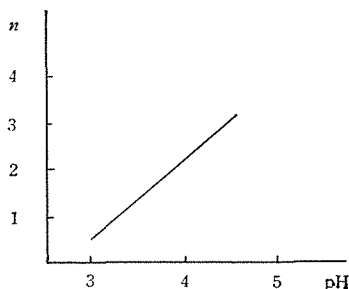
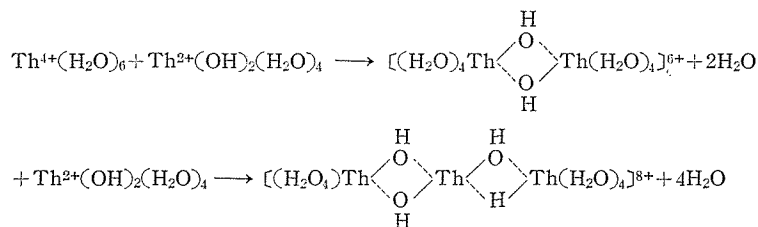


Fig. 2. The hydroxyl number of thorium as a function of pH.

Olation and oxolation. In the course of investigating the stability of colloidal metal hydroxides, Thomas⁵⁾ and his co-workers have concluded that the composition, formation, and precipitation of colloidal metal hydroxides might be explained in terms of olation and oxolation. According to their notations, hydrolytic products of thorium may be represented as follows.



Thomas has collectively called "olation" for such reaction. The existence

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of olation compounds and structure have been determined by Dobry *et al.*⁽⁹⁾ on colloidal thorium hydroxide prepared by dialysis of dilute thorium chloride. Viscosity, light-scattering, and electron microscopy studies indicate the particles in colloidal thorium hydroxide are thread-like with a diameter of about 18 Å and average length of 700 Å. The cross-section corresponds to boundless is perhaps 20 to 30 of the simple chains of unit particle as is illustrated in Fig. 3.

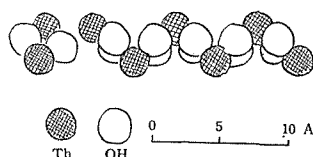
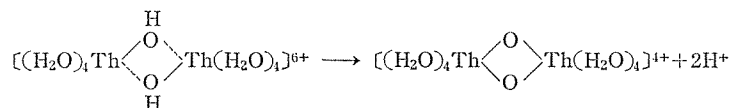


Fig. 3. The simple chain of colloidal thorium hydroxide.

The olation reaction might be expected to be reasonably rapid and Thomas, therefore, proposed the another reaction, which was referred to "oxolation", to account for the ageing of colloidal metal hydroxides. Concerning the colloidal thorium hydroxide, the oxolation process may be written as :



The essential differences of the olation and oxolation are distinguished by the generation of hydrogen ion and the reaction rate.

The time effect and the pH shifting phenomenon which were observed in pH titration of thorium may be explained by the results that were obtained here. That is to say, olation compounds (of thorium) which are formed in the earlier stage of pH titration of thorium change gradually into oxolation compounds liberating the hydrogen ion. When the titration ceases, the acidity of solution increases owing to the generation of hydrogen ion, and it is observed as the pH shifting phenomenon. The time effect of titration curve should be explained in the same manner, the elucidation of which is under study.

The results of Experiment 1 are very important on the estimation of solubility of thorium hydroxide especially on the ageing effect of thorium hydroxide in solution.

EXPERIMENT 2

According to the results of preliminary tests, it was found that the acidity and the time of ageing controlled the solubility of thorium hydroxide in aqueous solution. Therefore, sample solutions were prepared not only varying the acidity of solution but also time of ageing.

The procedures of the measurement and preparation of the samples are as follows.

Parparation of the sample. Thorium nitrate solution of 3×10^{-3} mole was adjusted to about 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0 in pH value with sodium hydrox-

ide solution and was allowed to stand for 0.5, 1, 2, 3, 7, 30 and 100 days in an air-tight polyethylene bottle, respectively. After standing, every solution was filtered with the filter paper (Tôyô-Roshi, No. 5C), and the acidity of the filtrates was measured with a glass electrode pH meter.

Method of estimation. The amount of thorium in each filtrate was determined colorimetrically with *o*-arsonophenylazo-chromotropic acid as a colorimetric reagent⁷⁾.

The results of Experiment 2 are given in Table 1.

Table 1. The solubility of thorium hydroxide.

Time of Ageing	pH	Th ⁴⁺ /l 1mg	pH	Th ⁴⁺ /l 1mg	pH	Th ⁴⁺ /l 1mg	pH	Th ⁴⁺ /l 1mg	pH	Th ⁴⁺ /l 1 μg
30 Min.	5.60	1,240	6.10	175	6.40	35.6	6.90	4.32	7.60	311
0.5 Day	4.70	805	5.00	96.8	5.50	13.7	6.00	1.40	6.40	160
1 "	4.25	235	4.60	35.0	5.10	8.02	5.70	0.625	6.23	109
2 "	4.05	88.1	4.45	13.4	4.95	4.40	5.50	0.442	6.20	78.5
3 "	4.00	45.2	4.30	11.4	4.90	2.16	5.50	0.234	6.10	53.7
7 "	3.80	16.1	4.30	3.72	4.70	1.14	5.50	0.161	6.10	50.7
15 "	3.75	8.9	4.30	1.53	4.70	0.57	5.55	0.108	6.10	46.4
30 "	3.75	4.4	4.25	0.68	4.70	0.394	5.45	71.7 μg	6.10	44.3
100 "	3.75	4.3	4.25	0.59	4.70	0.347	5.40	68.5 μg	6.05	34.5

DISCUSSION

The relationship between the acidity of solution and the amounts of thorium in solution can be expressed* as :

$$\log[\text{Th}^{4+}] = \log P + 56 - 4\text{pH} \quad \dots\dots\dots(8)$$

where $[\text{Th}^{4+}]$ is the equilibrium concentration of thorium ion and P is the solubility product of thorium hydroxide.

In Fig. 4, a comparison is made between two solubility curves: the solid curve was obtained from the equation (8) and the broken one from the values in the last row in Table 1.

A remarkable disagreement was observed between the two solubility curves. Furthermore, the experimental solubility curve was not obtained as a straight

* Equation (8) can be driven as follows.

Solubility product is defined as :

$$[\text{Th}^{4+}][\text{OH}^-]^4 = P,$$

this relation can be written

$$\log[\text{Th}^{4+}] + 4 \log[\text{OH}^-] = \log P,$$

and taking

$$\log[\text{OH}^-] + \log[\text{H}^+] = -14,$$

so that

$$\log[\text{OH}^-] = -14 - \log[\text{H}^+] = -14 + \text{pH},$$

we have

$$\log[\text{Th}^{4+}] = \log P + 56 - 4\text{pH}.$$

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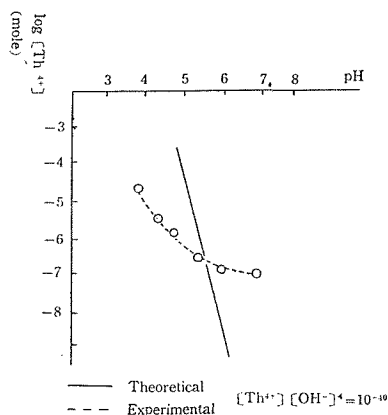


Fig. 4. The Solubility curve of Thorium hydroxide.

line but as a concave curve.

This result indicates that the equilibrium of thorium ion and hydroxyl ion is not so simple as Equation 8 (or Eq. 2) but more complicated one.

In order to explain this curious appearance of the experimental solubility curve, the information of the hydrolytic behaviours of thorium became indispensable.

As mentioned in the preceding chapter, colloidal thorium hydroxide and other hydrolytic species of thorium in aqueous solution gradually change into thorium hydroxide precipitation through olation and oxolation. Consequently, the total amounts of thorium in solution gradually decrease its concentration as time goes on. This phenomenon is generally accepted as ageing of precipitation. On examining the values in Table 1, the gradual decrease in solubility value and the increase in acidity are observed. Furthermore, the influence of acidity on the solubility value is negligibly small (experimental solubility curve is almost horizontal) in the pH range of 6 to 7.

These results lead to the conclusion that the solubility value (in Table 1) do not represent the amounts of pure thorium ion in solution but the total amounts of thorium existing as colloidal or hydrolysed state in solution.

CONCLUSION

Solubility of thorium hydroxide was determined colorimetrically and the following conclusions were obtained.

- 1) Solubility of thorium hydroxide is greatly affected on ageing.
- 2) Almost all parts of thorium exist as colloidal or hydrolyzed state in neutral pH range of aqueous solution.

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